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X-ray and IR studies of crystallinity and disorder in chemically treated coir fibre

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Abstract : The degree of crystallinity and disorder parameter of untreated and alkali and heat treated coir fibres have been measured by applying the wide-angle X-ray diffraction (WAXD) method of Ruland and Vonk The crystallinity measurement has been supplemented by estimating the crystallinity index using an IR technique. The results appear to suggest the presence of highly distorted crystalline regions that are first affected by lower concentration (5%) of alkali The lattice transformation from cellulose I to cellulose II is restricted with continued decrystallization Both the methods show that, in general, crystallinity decreases with concentration of alkali and rise of temperature

Keywords : X-ray and IR studies, coir fibre, crystallinity and disorder

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1. Introduction

It is well established that the degree of order existing in the arrangement of atoms in a solid plays the key role in deciding its major physical and mechanical properties [1,2]. However the poorly crystalline and distorted materials produce X-ray diffraction patterns which are very weak and broad [3] and hence unsuitable for measurement with accuracy as demanded by the usual X-ray line broadening techniques for X-ray characterization. Consequently, usual line profile analysis can not be applied for defect characterization (size, strain, layer disorder *etc.*) in this type of poorly crystalline multiphase polymeric systems. The problem is made still more complicated by the presence of several types of lattice disorder, whose occurrence is very common in this type of poorly crystalline natural fibres polymer like coir. These defects are broadly classified as distortion of the first kind and second kind [4]. While in the first kind, the long range order is preserved, the second kind, which is

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prevalent in natural fibres, destroys the long range order and affects the X-ray scattering significantly.

For characterizing this type of distorted biopolymer, the concept of 'degree of crystallinity' as a gross physical property, has very rightly been introduced. Degree of crystallinity which can be evaluated from the weak X-ray pattern constitutes a very important physical parameter which influences most of the physical and mechanical properties of the polymeric sample. X-ray methods based on crystallinity have been applied successfully for characterization of several polymeric samples [4–9]. Recently, Sao [10] have made an in-depth study of crystallinity and disorder in untreated and alkali treated ramie fibre by applying the method due to Ruland [11,12] and Vonk [13] and obtained several valuable information on the structural behaviour of ramie under various treatments. Unlike all the earlier empirical methods of determining crystallinity from the observed intensity [4,5], Ruland method is based on solid theoretical foundation and takes care of defects of both kinds–including thermal vibration.

Besides X-ray diffraction, recently IR spectra have been used by several workers for investigating structural characteristics and 'Crystallinity Index' in cellulosic [14–18] and lignocellulosic [19,20] fibres like coir. Crystallinity Index has been estimated by the ratio of the absorption bands at 1429 cm^{-1} and 893 cm^{-1} following O'Connor *et al* [21] and the results have been found to be in good agreement with the measured values of crystallinity by X-ray method.

It appears that no attempt has been made to date to study the crystallinity and disorder in coir by Ruland method, supported by the IR method. Hence, the present work was undertaken to make a systematic study of crystallinity and disorder in a native coir sample under different conditions.

2. Theoretical basis of X-ray method

The present investigation uses the method of Ruland [11,12] and Vonk [13]. The crystalline fraction x_c in the sample is given by

$$x_c = K \frac{\int_{s_0}^{s_p} s^2 . I_c(s) . ds}{\int_{s_0}^{\infty} s^2 . I(s) . ds}. \qquad (1)$$

Here $s = 2\sin\theta / \lambda, 2\theta$ is the scattering angle and λ, the wavelength of X-ray radiation. I and I_c represent, respectively, the intensity of coherent scattering by the sample and the coherent intensity scattered from the crystalline phase. The coefficient K takes care of the loss in intensity due to lattice imperfection and is given by

$$K = \frac{\int_{s_o}^{s_p} s^2 . \bar{f}^2 . ds}{\int_{s_o}^{s_p} s^2 . \bar{f}^2 . D . ds}. \tag{2}$$

where $\bar{f}^2$ is a mean square atomic scattering factor for the polymeric sample. D is the lattice imperfection factor. S_o and S_p represent the lower and upper limit of integration of the angular range.

If only thermal motion is involved, the D function is identical with an isotropic Debye-Waller factor. According to Ruland, all kinds of disorder can be lumped together in one Gaussian lattice-imperfection factor given by

$$D = \exp(-ks^2), \tag{3}$$

where $$k = k_t + k_1 + k_2, \tag{4}$$

k_t accounts for thermal motion, k_1 for other disorders of the first kind, and k_2 for disorders of the second kind.

Following Vonk [13] eq. (1) can be written as

$$R(s_p) = (1/x_c) + (k/2x_c)s_p^2, \tag{5}$$

where K has been approximated as

$$K = 1 + (k/2)\, s_p^2 \tag{6}$$

and

$$R(s_p) = \frac{\int_{s_o}^{s_p} s^2 . I(s) . ds}{\int_{s_o}^{s_p} s^2 . I_c(s) . ds}. \tag{7}$$

Thus, x_c and k can be calculated from the intercept and slope of the linear plot of $R(s_p)$ and S_p^2 using eq. (5).

3. Experimental

Bristle retted fibres were obtained by the courtesy of Central Coir Research Institute, Allepey, Kerala, India. The fibres were cut to small pieces, combed and cleaned, and then treated with different concentration of aqueous NaOH solution for two hours at each concentration at room temperature. A portion of this was thoroughly washed with distilled water to remove alkali to obtain mercerized fibre. Another portion was air-dried without washing to obtain soda-cellulose coir fibre which was carefully pressed to remove excess of alkali. For thermal treatment, the fibres were heated for two hours at each different temperature under vacuum (10^{-2} Torr). The treated fibres were powdered by prolong grinding in an agate mortar and pestle and finally sieved through a screen of 200 mesh.

The X-ray diffractograms of the samples were recorded in a Philips X-ray diffractometer (PW 1710) covering the entire detectable angular range spanning between 5° (2θ) to 90° (2θ) using filtered CuK_α radiation at 35 kV and 30 mA. IR spectra were taken by using Perkin Elmer spectrometer at a resolution of 2.4 cm^{-1}. The chemical composition [22] of the coir fibre under different treatments was carried out at CDRI, Lucknow on the basis of which incoherent scattering was calculated. The X-ray scattering curve of coir fibre heated to 350°C for two hours was taken as amorphous standard for all samples.

4. Results and discussion

X-ray diffractograms of native and alkali treated coir fibres exhibit only the well known cellulose-I pattern in contrast to other cellulosic fibres like ramie and cotton which show both cellulose I and cellulose II. Most likely the presence of lignin prevents the lattice transformation from cellulose I to cellulose II in this lignin rich sample [23]. The appearance of additional peaks in the diffractograms of air-dried soda-cellulose sample indicates the formation of soda-cellulose complex. Figures 1 and 2 show plots of $s^2 I(s)$

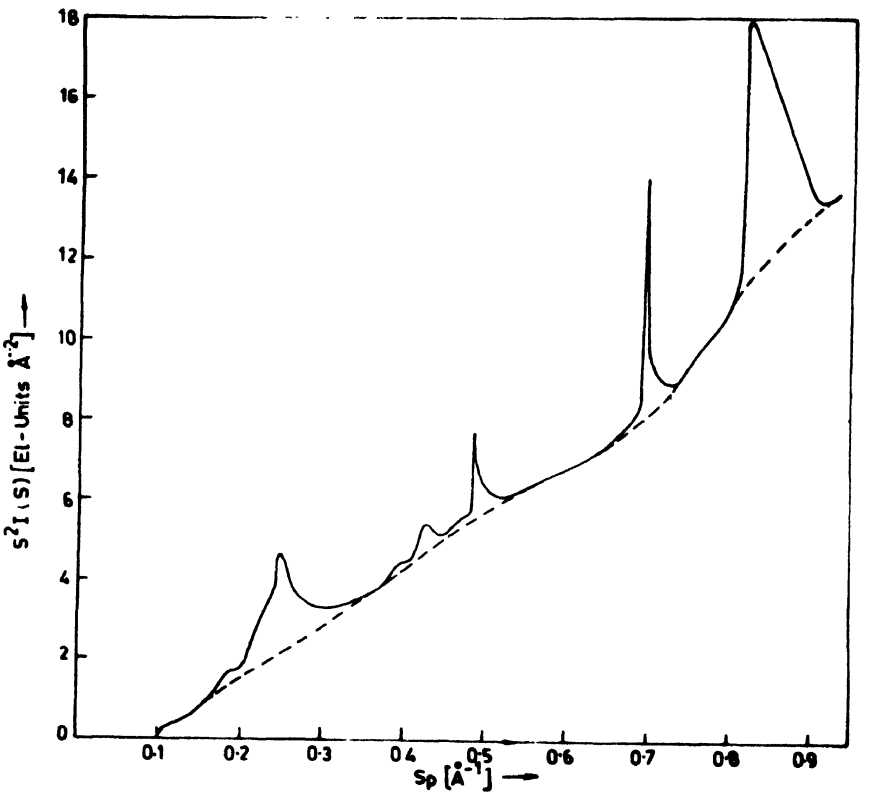

Figure 1. Plot of $s^2.I(s)$ *versus* s_p for 15% mercerized sample

versus s_p and $R(s_p)$ *versus* s_p^2 respectively for 15% mercerized sample. (Figure 3 shows the IR spectra of the same sample). The results of the measurement of crystallinity and

distortion under different treatment are given in Table 1. The table also gives the crystallinity index calculated from some selected bands of IR spectra. It is observed from

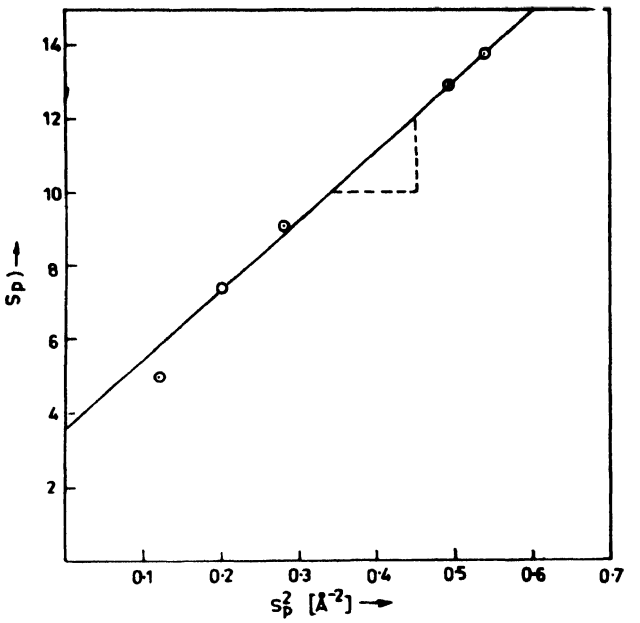

Figure 2. Plot of $R(s^{II})$ *versus* s_p^2 for 15% mercerized sample

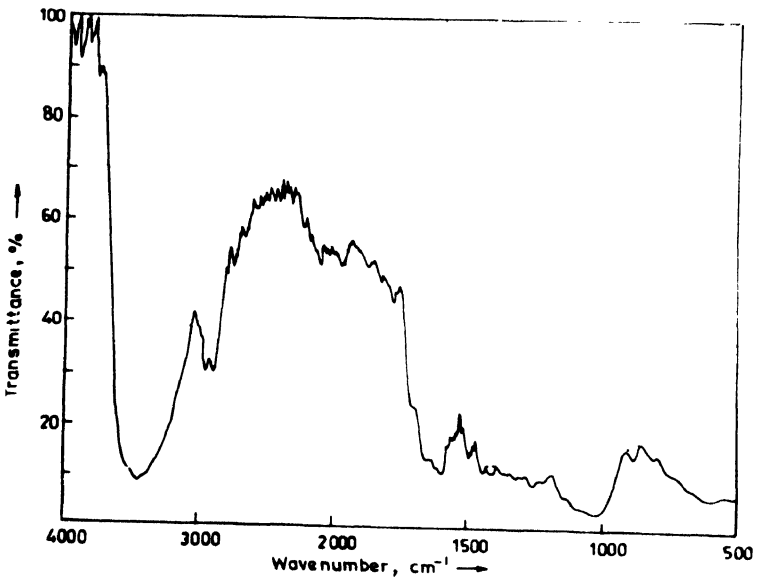

Figure 3. IR spectra of 15% mercerized sample.

Table 1 that the degree of crystallinity (x_c), barring an initial increase at 5% NaOH, in general decreases with increase in concentration. However, from 15% onward, the decrease

in x_c with concentration tends to be marginal. The disorder parameter (k) initially decreases abruptly to a minimum value around 5%. Thereafter, the increasing trend sets in which

Table 1. Variation of degree of crystallinity (x_c), distortion (k) and crystallinity index (C I) for coir fibre

Kind of treatment		X-ray analysis		IR analysis		
		x_c%	$k(A^2)$	CH_2 band (cm^{-1})	C_1-H band (cm^{-1})	CI
	Raw	46 50	13 00	1433	901	0.57
Mercerized	5%	51 90	1 41	1421	897	0 62
	10%	36 30	4 35	1418	901	0 57
	15%	27 70	10 07	1420	895	0.50
	20%	27 00	10.30	1425	894	0 40
	30%	26 30	7 42	1423	895	0.33
Soda-cellulose	15%	27 30	11 34	1466	849	0 44
	30%	25 90	12.27	1459	859	0 29
Heat-treatment	27 C	46 50	13 00	1433	901	0 57
	65 C	45 84	4 84	1427	903	0 50
	120 C	40 00	12 26	1425	896	0 44
	200 C	35 70	4 80	1457	852	0 37
	300 C	33 33	6 97			

tends to continue up to 20%, beyond which the distortion decreases considerably at 30% concentration. Compared to the washed samples, the values of x_c are found to be slightly lower while that of disorder considerably higher in air-dried alkali coir fibre. Interestingly, the heat-treated sample shows a steady decrease of crystallinity with rise of temperature. Contrary to expectation, the variation of distortion appears to be somewhat irregular with a sharp initial decrease around 65° C followed by a steep rise to a maximum value at 120°C. However, the values of k corresponding to 200 and 300°C are much lower than the value at 120°C.

Although the values of crystallinity index as obtained from IR measurement, in general, are higher than the corresponding values of x_c for all samples, interestingly the variational patterns followed by both sets of results, as expected, agree quite satisfactorily, as revealed in Figures 4 and 5. The marginal difference in the values may be due to the underlying differences in the physical meaning of the two different parameters used.

The abrupt decrease in disorder parameter (k) associated with increase in x_c at 5% NaOH treatment may be explained by assuming the existence of the intermediate order which may be termed distorted crystalline regions [24]. Verma *et al* [25] also observed initial increase in crystallinity at low concentration of alkali in coir fibre lending further

support to the idea of existence of intermediate states in this ligno-cellulosic system. Beyond 5% concentration, the alkali may cause further disorder in these regions increasing the amorphous fraction and disorder factor k due to the removal of hemicellulose and lignin [26,27]. This process continues unabated without any lattice transformation till 30% where

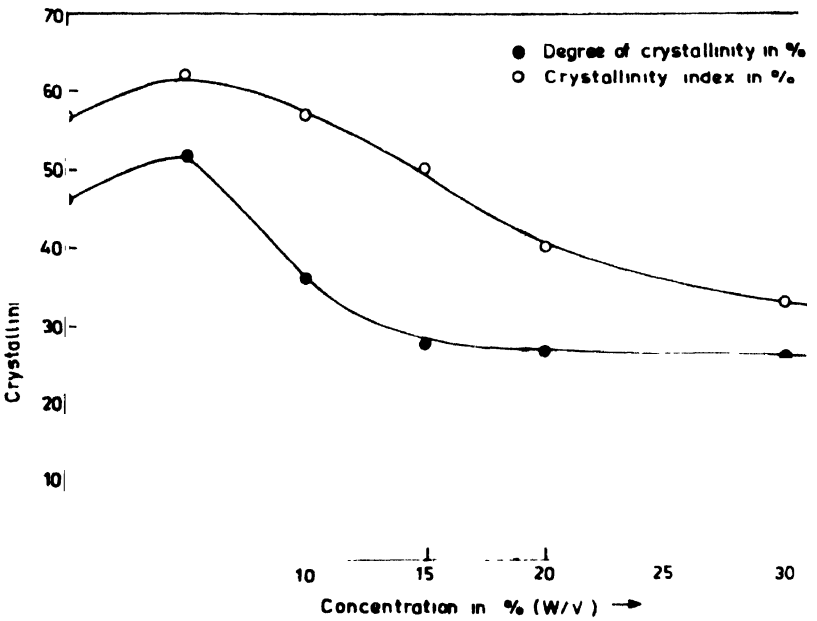

Figure 4 Plot of crystallinity *versus* concentration by XRD and IR methods

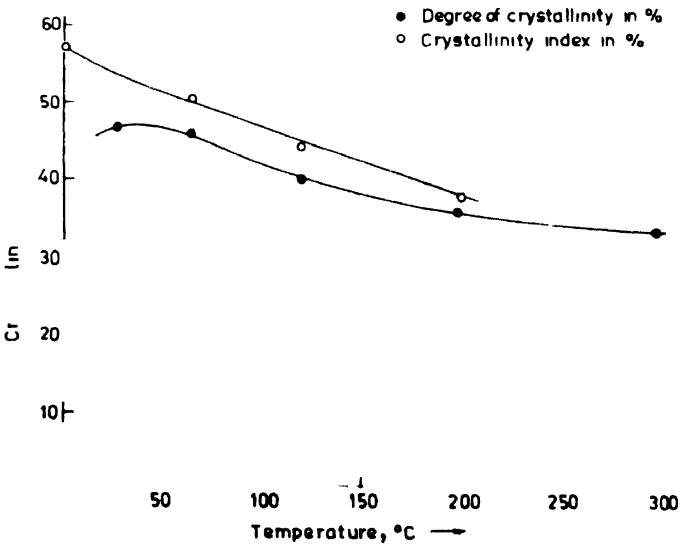

Figure 5 Plot of crystallinity *versus* temperature by XRD and IR methods

the disorder decreases appreciably. At this high concentration of alkali there is further removal of the residual lignin and complete removal of hemicellulose, releasing the strain

from the lattice. The moderate decrease in the value of disorder at this stage may be attributed to the depolymerization into the stress free crystallite units. The conversion into cellulose-II involves rotation of *D*-glucose residue about the glycosidic link and a rearrangement of hydrogen bonding network [28,29]. The prevention of the formation of cellulose II can perhaps be explained in the same way as was done by Revol and Goring [23] on the basis of lamellar microfibrillar model in the case of lignin rich wood. The presence of lignin, which is layered between the microfibrillar ribbons and prevents the molecules in the microfibril of opposite polarity getting together during mercerization process [23] is responsible for continued decrystallization without lattice transformation. An alternative explanation may also be attempted for this resistance to conversion from cellulose I to cellulose II by considering the model of Nishimura and Sarko [30]. According to these authors, the lattice transformation starts in the oriented amorphous region lying between adjacent well ordered crystallites. The absence or presence of insufficient quantity of oriented amorphous region owing to the complicated nature of its composition, coupled with the difficulty the alkali faces to reach the region penetrating the crystallites, may be responsible for restricting the conversion to cellulose II. In the air-dried alkali coir fibre (Table 1), the crystallinity is seen to be marginally lower and distortion parameter higher than in the corresponding washed samples. Assuming the existence of distorted crystalline regions, the presence of Na^+ ions in these regions is quite likely to disturb further the structural state and consequently increases k value and lowers x_c values. At higher concentration of 30% NaOH, the Na^+ ions penetrate the inter-chain space in the crystalline regions resulting in the formation of soda-cellulose complex. The lower value of x_c in the air-dried soda-coir fibre compared to that of the corresponding washed sample may be due to the highly disordered structure of soda-cellulose.

The sharp decrease in the value of distortion parameter associated with moderate decrease in crystallinity value for the heat treated coir fibre around 65°C, indicates once again the presence of highly distorted crystalline regions as discussed earlier. These regions seem to be first affected resulting in the decrease of k-value. The increase in k-value and decrease in x_c-value around 120°C may be due to dislodging of water molecules during which process the ligno-cellulosic system is rendered more distorted because of setting up stresses during drying. The lower distortion value at 200°C may be due to complete dehydration followed by degradation into smaller and less disordered molecules. The results thus indicate that in both the cases, namely alkali and heat treatments, the highly distorted crystalline regions in the fibre are first affected. The decrease in crystallinity and consequent increase in distortion parameter above 200°C may well be attributed to gradual dehydration followed by fragmentation of crystalline domains owing to thermal degradation. However, the variation of k is very unsystematic and is rather too difficult to explain satisfactorily on the basis of the present model. The above results broadly support the observations of earlier workers that the degradation in the initial stage is associated with the disordered regions and thereafter the decomposition in the crystalline region begins [31,32].

The values of crystallinity index from IR analysis are higher than those of the corresponding 'degree of crystallinity' values calculated from X-rays. This may be due to the identical bands of hemicellulose and cellulose used in the technique, where hemicellulose is a non-crystalline component of the fibre.

5. Conclusions

The following broad conclusions may be summarized from the above studies :

(i) The simple two-phase model of completely ordered and disordered phases has little validity for coir-cellulose. The existence of intermediate order regions (paracrystalline) such as highly distorted crystalline regions, has to be considered for a satisfactory explanation of the phenomenon of swelling or low temperature thermal degradation.

(ii) In general, the crystallinity decreases both, on alkali and thermal treatments as observed by X-ray and IR methods.

(iii) The soda-cellulose treated coir fibres are more decrystallized and disordered than the corresponding mercerized samples. This may be due to penetration of Na^+ ions into the inter-chain space of the cellulose molecules forming soda-cellulose complex.

(iv) That the distortion in poorly crystalline coir fibre does not vary systematically and hence cannot be explained fully on the basis of any one of the existing models.

However, owing to the complex nature of this structurally disordered multi-component natural lignin rich polymeric system and the associated experimental limitations, it has not been possible to offer satisfactory explanation to every finer change. Attempts have been made to present an average behaviour of the material under different conditions.

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